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on the Hydrolysis Kinetics of Alkylketene Dimer

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The Effects of Inorganic Salts and Precipitated Calcium Carbonate Filler on the Hydrolysis Kinetics of Alkylketene Dimer

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ABSTRACT

The effects of inorganic salt, precipitated calcium carbonate (PCC), pH and temperatures on the kinetics of the hydrolysis of alkylketene dimer (AKD) were studied using the FT-IR method. It was found that the common dissolved salts have no obvious effect on the hydrolysis kinetics, while the wet-end additives such as alum and PCC have mixed effects. The temperature and pH could accelerate the hydrolysis of AKD, which supports previous published results. Alum does not have a significant effect under acidic conditions, but shows strong interaction with AKD under alkaline conditions. Both bicarbonate ion and PCC have a significant catalytic effect on the hydrolysis of AKD, and the mechanism of this catalytic effect is discussed.

Keywords: Alkylketene dimer, salt concentration, sizing, kinetics, hydrolysis.

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INTRODUCTION

Alkylketene dimer (AKD) based sizing agents have been widely used in the paper industry. It is generally accepted that AKD reacts with cellulose hydroxyl groups to form a β -keto ester linkage during papermaking. The formation of the β -keto ester bond in AKD sized paper was proven by infrared and solid state carbon NMR, calorimetry and solvent extraction [1,2] and was found to be vital for effective sizing.

In addition to reacting with hydroxyl groups of cellulose, AKD is also subjected to hydrolysis by water. This can be detrimental to sizing because the hydrolysis reaction produces an unstable β -keto acid which then decarboxylates to form a ketone, as shown in Figure 1. This ketone is not capable of reacting with hydroxyl groups, and, therefore, would be expected to detract from sizing efficiency.

Studies on AKD sizing and hydrolysis have been carried out before. Higher temperature and pH were shown to accelerate both the rates of esterification and hydrolysis reactions [3]. Lindström [4] found that the presence of bicarbonate ion (HCO_3^-) can increase AKD to function as an internal sizing agent and suggested that the bicarbonate ion is a catalyst for the esterification reaction. Roberts [5] observed a decrease in sizing efficiency when AKD was used in the presence of high levels of alum at pH between 4.4 to 5.8. On the other hand, Wortley [6] reports that alum use at lower levels in alkaline AKD systems by careful application can actually improve sizing. The interactions between AKD and precipitated calcium carbonate (PCC) fillers have been studied by the solid-state carbon NMR method [1]. It is reported that AKD can react with both $\text{Ca}(\text{OH})_2$ and CaCO_3 and then decompose to ketone. The extent of this

transformation is directly related to surface area and calcium hydroxide concentration in the filler.

Reducing fresh water in a paper machine remains another important concern to the papermakers. Regardless of the reason for closure, detrimental substances will increase in the white water. The buildup of dissolved electrolytes and contaminants in closed water results in a significant increase in conductivity, anionic trash content, water hardness, sticky deposition, and cationic polymer demand. These dissolved and colloidal substances may lead to a reduction in the efficiency of chemical additives, such as sizing and retention agents. Although many experiments have been done on the mechanism of sizing development of AKD at various conditions, the effects of detrimental materials on the AKD hydrolysis kinetics have not been reported. This paper focuses on the hydrolysis kinetics of AKD at different wet-end conditions, particularly at different concentrations of salts and PCC fillers. The possible interactions between AKD and other wet-end additives are also discussed.

EXPERIMENTAL

Materials

Both AKD emulsion (15% AKD) and pure AKD pellets were obtained from Hercules Inc. Precipitated calcium carbonate (Albacar[®]HO, Specialty Mineral Inc.) was a scalenohedral calcite product with an average size of 1.3 μm and specific surface area

of 12 m²/g. Other inorganic salts and organic solvents were from Aldrich. All materials were used as received.

Hydrolyzed AKD used for calibration was prepared as follows. Pure AKD pellets (2 g) in 10% sodium hydroxide solution (50 ml) were heated at 60°C for 6 hours. After cooling, the mixture was adjusted to pH 4-6 by adding 10% hydrochloric acid and then extracted with chloroform (50 ml) three times to give hydrolyzed AKD (1.8 g) as a white solid. FT-IR spectrum of the hydrolyzed AKD confirms the disappearance of 1848 cm⁻¹ C=O stretching band of AKD.

Physical property measurements

FT-IR spectra were recorded on a Nicolet Magna-IR Spectrometer 550 using KBr discs. About a 1-mg sample was used for each KBr disc (0.5 g).

Hydrolysis kinetics tests

A mixture of AKD emulsion (40 ml) and a required amount of additives was put in a 50-ml plastic tube, and AKD emulsion concentration was adjusted to 100 ppm at desired pH. The mixture was then stirred in a water bath at controlled temperature. After a predetermined period, 10 ml of the reaction mixture were taken out and cooled immediately in an ice-bath and the final pH was measured. Hydrochloric acid was added to reduce the pH to 2-3. The mixture was then extracted with chloroform (15 ml) three times, and the combined chloroform layer was dried with anhydrous sodium sulfate. After filtration, the chloroform solution was evaporated on a rotary evaporator and the

solid was dried under vacuum for ten hours. The extent of hydrolysis was determined by FT-IR measurements.

RESULTS AND DISCUSSION

Method of AKD analysis

There are several methods discussed in the literature for the analysis of AKD hydrolysis. Conventional gas-liquid chromatography (GLC) [7] gives quantitative information about AKD-related compounds, but does not discriminate between hydrolyzed and unhydrolyzed species. The UV method [8] is difficult to process because it involves complicated chemical reaction and separation processes. The FT-IR method used by Marton [3] was shown to be simple and could also give a quantitative estimation of still-reactive diketenes.

Figure 2 shows the FTIR spectra of a mixture of hydrolyzed and unhydrolyzed AKDs. The α peak at 1848 cm^{-1} indicates the C=O stretching band of unhydrolyzed AKD and thus can indicate the active-AKD present in the mixture. The β peak at 1468 cm^{-1} indicates the $-\text{CH}_2-$ bending band of both hydrolyzed and unhydrolyzed AKD, and the value can be regarded as a constant. The fraction of unhydrolyzed AKD in the mixture can therefore be determined by the ratio of $R (= \alpha/\beta)$.

The standard calibration curve of R as a function of unhydrolyzed AKD in the mixture was first measured using different mixtures of hydrolyzed and pure AKDs. Figure 3 shows that although the relationship between R and the fraction of unhydrolyzed

AKD is not a perfect line, the graph can still be used as a reliable calibration curve. In this study, the fractions of unhydrolyzed AKD at different conditions were calculated using the calibration curve shown in Figure 3.

In order to study the kinetics of AKD hydrolysis at different conditions, the cationic AKD emulsion used in this study was analyzed immediately after it was received, and the results indicated that the original AKD emulsion from the manufacturer contained 22% of hydrolyzed AKD when they reached customers.

Temperature and pH effects on the hydrolysis of AKD

Marton [3] reported that high temperature and pH accelerated the hydrolysis of AKD in water. In order to study the effects of other factors on the hydrolysis kinetics, the effects of temperature and pH on the AKD hydrolysis were also examined in this study. Figure 4 shows that the hydrolysis of AKD was accelerated at elevated temperatures. At the starting pH 8.3, the AKD had undergone 48% hydrolysis (including 22% from original sample) when temperature was increased to 50°C, whereas no detectable change in hydrolysis of AKD (around 22% AKD hydrolysis as original sample) was observed at 22°C after a five-hour hydrolysis test.

Figure 5 shows that the AKD hydrolysis is accelerated dramatically with increased pH. After five hours at 50°C, 75% of total AKD had been hydrolyzed in the solution with a starting pH of 10.4, whereas only approximately 48% of AKD (including 22% from original sample) had been hydrolyzed in the solution with a starting pH of 8.3. Compared to the hydrolysis under alkaline conditions, no further hydrolysis (comparing to the original sample 22%) was observed at pH 4.8 in the five-hour period at the same

temperature. These results agreed well with the previous results [3], and it was suggested that a significant amount of hydrolyzed AKD may be present in an alkaline papermaking furnish, which strongly depends on the pH, temperature, and residue time of AKD in the furnish. To reduce the hydrolysis of AKD, the addition point of AKD should be close to the headbox. Figure 5 suggests that comparing to the original sample, about 11% more of the original AKD had been hydrolyzed in a furnish of pH 8.3 at a papermaking temperature of 50°C if the residue time was longer than an hour. The hydrolysis rate is even faster if PCC is used as a filler. The effect of PCC on the AKD hydrolysis will be discussed later.

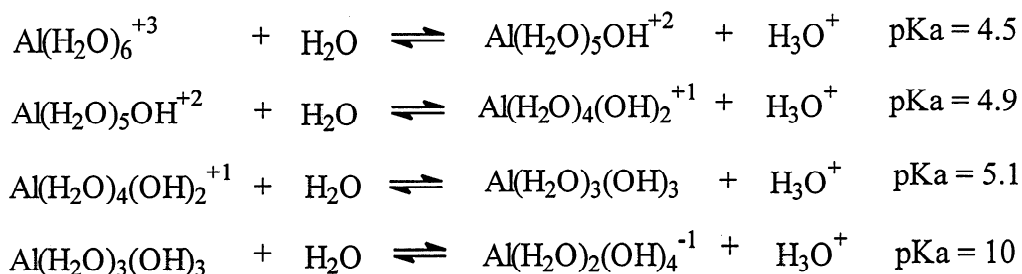
The effect of dissolved inorganic salts

The build up of inorganic substances in whitewater may affect the AKD hydrolysis rate. This effect was examined in this study using Na₂SO₄, CaCl₂, NaCl and their combinations as inorganic salts. As shown in Figure 6, the inorganic salts of sodium sulfate, sodium chloride and calcium chloride in water were found to have no significant effect on AKD hydrolysis even at very high concentrations. This suggests that the hydrolysis of AKD in a closed white water system are not mainly caused by increased salt concentration.

The effect of alum on the hydrolysis of AKD

The usefulness of aluminum compounds in alkaline papermaking has been greatly debated. [5,6] This is due to alum's unique chemical and physical properties. The alum complex reactions show that alum mainly exists as soluble ions $(Al(H_2O)_6)^{+3}$,

$\text{Al}(\text{H}_2\text{O})_5\text{OH}^{+2}$ and $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^{+1}$ in an acidic water solution but dominantly exists as insoluble $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3$ in a neutral to slightly basic water solution, as shown below.



Although alum will lose its cationic properties at high pH, many alkaline paper mills still use alum as a wet-end additive. Therefore, the effect of alum on the AKD hydrolysis at different pH values should be studied. This effect is shown in Table 1

It can be seen from Table 1 that at pH 4.8 and 50 °C alum addition up to 280 mg/L has no significant effect on the hydrolysis of AKD compared to hydrolysis without alum addition after 5-hour reaction. However, the interaction between alum and AKD under alkaline conditions was much more complicated than that under acid conditions. For the AKD hydrolysis at alkaline conditions, the pH of AKD emulsion was first adjusted to pH 8.0, then the required amount of alum was added to the emulsion. Large aggregates were gradually formed in the mixture after the addition of alum. After a 5-hour reaction at 50°C, the mixture was adjusted to pH 2-3 by hydrochloric acid addition and then extracted with chloroform. Surprisingly, the aggregates formed during the reaction could not be dissolved even at pH 2-3, and no AKD (either hydrolyzed or unhydrolyzed AKD) could be extracted from the reaction mixture when the amount of alum used was higher than 140 mg/L. In order to understand the mechanism of the reaction between AKD and alum at alkaline pH conditions, the same process was also

applied to alum solutions in the absence of AKD. It was found that the aggregates of aluminum oxides formed at room temperature could be easily dissolved when pH was reduced to 2-3 by addition of hydrochloric acid. However, those aggregates formed at pH 8.0 and 50°C after a 5-hour reaction could not be redissolved. The insoluble properties of aged aluminum oxides under acidic conditions may result from the dehydration and the change of the crystal structure of aluminum oxides at high temperature. The above phenomena suggest several possible reactions between alum and AKD at alkaline conditions and high temperature. First, AKD may be physically entrapped in the aggregates of aluminum oxides during the formation of the aggregates. Because the aggregates of aged aluminum oxides are insoluble even at pH 2-3, the entrapped AKD could not be extracted even using a good solvent. Second, AKD molecules may form complexes with aluminum oxides at high pH. If this is the case, the strong chemical bonds between aluminum oxides and AKD protect the AKD from extraction. Third, the physically adsorbed AKD on the surface of aged aluminum oxides may also protect the AKD from extraction. Although the real mechanism of AKD-alum interaction has not been investigated, the results shown in this study indicated that AKD could be strongly bonded by alum aggregates at alkaline conditions.

When the amount of alum used was low, at 55 mg/L, a small amount of AKD-related compounds could be recovered. Analysis of this recovered sample indicated that 69% of total AKD had been hydrolyzed after a 5-hour reaction at pH 8.0 and 50 °C. However, since most AKD-related compounds could not be recovered from this system, the result may not reflect the real hydrolysis rate.

Regardless of the mechanisms involved in the reaction between AKD and alum, the presence of large amounts of alum will be detrimental to sizing using AKD under basic conditions. The adsorption effect of alum to AKD may make it difficult for AKD to spread on the surface of fiber uniformly, and the possible covalent bonds between AKD and aluminum will further prevent reactions between AKD and fibers. More studies, such as effects of reaction time, addition order and temperature on the complex formation and sizing development are needed to clarify the interactions between aluminum and AKD under alkaline reaction conditions.

The hydrolysis of AKD in buffer and PCC solutions

AKD has been widely used as an alkaline sizing agent for PCC-containing paper products. Large quantities of PCC act as a buffer to maintain a narrow pH range in a pulp furnish. This study found that a slight drop in pH (~1 unit) occurs after the hydrolysis reaction if the reaction solution was unbuffered. Since the AKD hydrolysis rate is very sensitive to the solution pH, the effect of buffer solutions and PCC on the hydrolysis of AKD was studied.

The buffer solutions used in this study include 0.1 M KH_2PO_4 / NaOH and 0.1 M NaHCO_3 / NaOH solutions, and their effects on AKD hydrolysis are shown in Figure 7. It can be seen that all of the buffer solutions accelerated the hydrolysis of AKD compared to the unbuffered solution at the same starting pH. But the results cannot be explained simply by the effect of pH. A parallel experiment that started at pH 10.4 and finished at pH 9.0 in the absence of a buffer showed a significantly lower hydrolysis level compared to those under buffered conditions. It has already been found previously that Na^+ , Ca^{2+} , Cl^- and SO_4^{2-} have no obvious effect on the hydrolysis of AKD; thus, the acceleration of

the hydrolysis rate in buffer solutions may be mainly contributed to anionic ions H_2PO_4^- , CO_3^{2-} and HCO_3^- .

To further study the anionic effect, the hydrolysis of AKD in different concentrations of sodium bicarbonate was investigated. It was found that the hydrolysis of AKD increased dramatically with the increase of the sodium bicarbonate concentration (Figure 8). This further confirmed the catalytic effect of the bicarbonate ion on the AKD sizing, which was studied previously [4], and also indicated the catalytic effect of the bicarbonate ion on the AKD hydrolysis.

It is interesting to note that the AKD hydrolysis rate significantly increased as the amount of PCC in the suspension increased, as shown in Figure 9, and the PCC showed a much higher catalytic effect on the AKD hydrolysis compared to that of sodium bicarbonate (Figure 8). It was observed from our experiment that even the most dilute PCC (57 mg/L) was not totally soluble in water at the hydrolysis temperature (50°C). Considering that calcium carbonate is almost insoluble ($K_{sp} = 3.36 \times 10^{-9}$ at 25°C) in water, it could only produce a very low concentration of anionic carbonate ions (5.8×10^{-5} mol/L, which is much lower than that produced by the sodium bicarbonate solution at the same concentration). Compared to the results obtained with the same concentrations of NaHCO_3 and PCC (see Figure 8), it could be concluded that PCC is a more effective catalyst for AKD hydrolysis than HCO_3^- . Since most PCC samples contain different contents of calcium hydroxide, both PCC and calcium hydroxide solid particles may contribute to the acceleration of AKD hydrolysis. However, it should be noted that the significant difference between AKD hydrolysis in an HCO_3^- solution and a PCC suspension should not be attributed to the effects of pH and dissolved anions

(carbonate and bicarbonate) because both systems were adjusted to the same pH in the experiments, and the theoretical calculation indicated that carbonate and bicarbonate concentrations in PCC suspension were much lower than that in NaHCO_3 solution.

The sizing mechanism of AKD using bicarbonate ion and calcium carbonate was reported previously. Lindström and Söderberge [4] found that the presence of bicarbonate ion can increase the sizing ability of AKD, and they further concluded that a catalytic effect of HCO_3^- as a proton-accepting base to increase nucleophilic attachment to the hydrogen atom of cellulose hydroxyl groups is the main cause of the increased sizing. Bottorff [1] provided description of the AKD sizing mechanism in CaCO_3 by using the solid-state carbon NMR technique. He suggested that AKD undergoes reaction with precipitate calcium carbonate and calcium hydroxide to produce an intermediate product, which decomposes to give diketone. He further concluded that this is the main reason for sizing loss.

Our experimental work suggests that the presence of bicarbonate ion, PCC and contained calcium hydroxide in PCC all contribute to AKD hydrolysis. Similar to the mechanism of AKD sizing suggested by Bottorff [1], we believe that AKD can react not only with the bicarbonate ion but also with the solid calcium carbonate and calcium hydroxide (contaminate in PCC), and then can decompose to diketone.

CONCLUSIONS

The AKD hydrolysis reaction was studied under different wet-end conditions. It was found that hydrolysis of AKD was accelerated at elevated temperatures and increased pH values. Although the closed mill white water contains buildup contaminants, the dissolved inorganic salts in the closed mill water do not significantly affect the AKD hydrolysis. The effect of alum is complicated. Under acidic conditions, alum showed no effect on AKD hydrolysis; but under basic conditions, alum strongly affected AKD hydrolysis rate, which may be detrimental to AKD sizing. The PCC showed an extremely high catalytic effect on AKD hydrolysis. This catalytic effect could also be detrimental to alkaline sizing as sizing loss may occur over time.

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Table 1. The effect of alum on the hydrolysis of AKD (100 mg/L).

pH	4.8				8.0			
Alum conc.(mg/L)	0	55	140	280	0	55	140	280
Temp. (°C)	50	50	50	50	50	50	50	50
Time (h)	5	5	5	5	5	5	5	5
Hydrolysis of AKD (%)	22 (the same as the original sample)				46	69	Form aggregates and no AKD could be extracted	

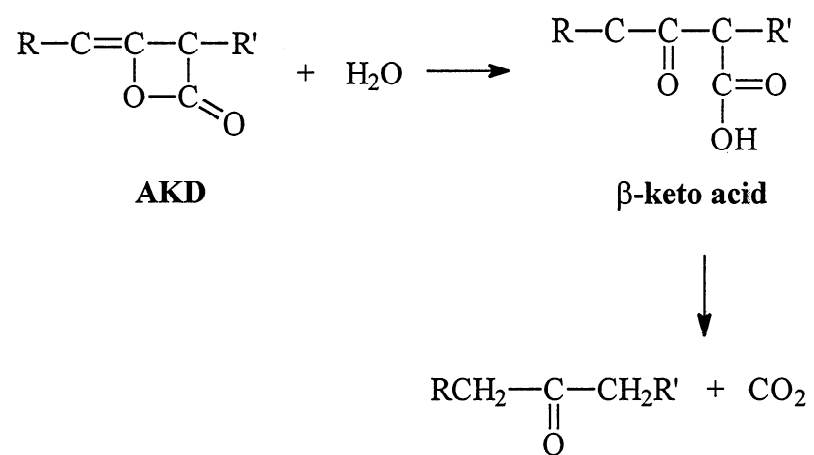


Figure 1. AKD hydrolysis reaction.

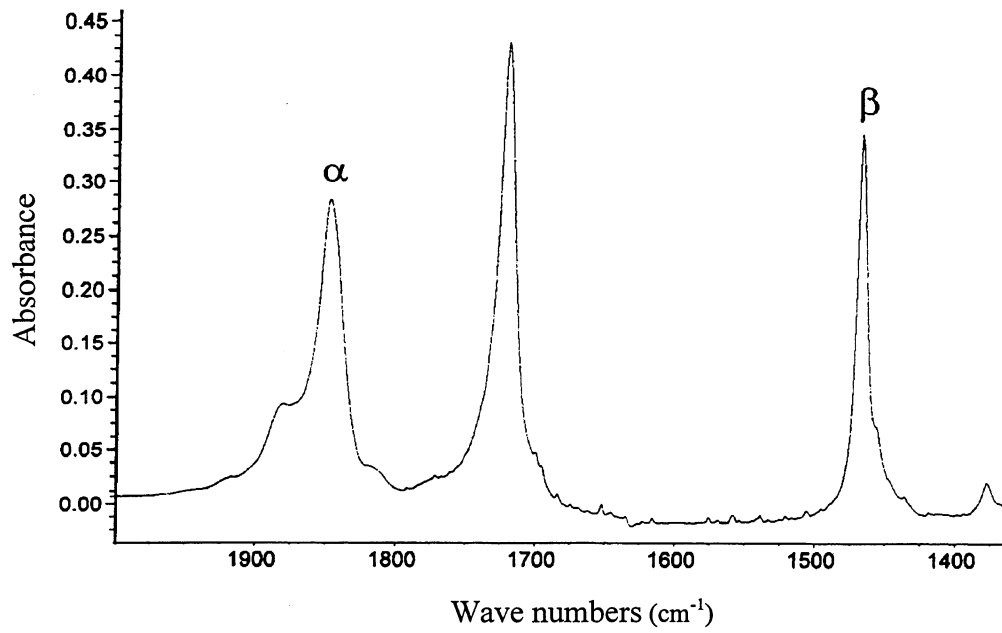


Figure 2. FT-IR spectrum of typical mixture of AKD and hydrolyzed AKD.

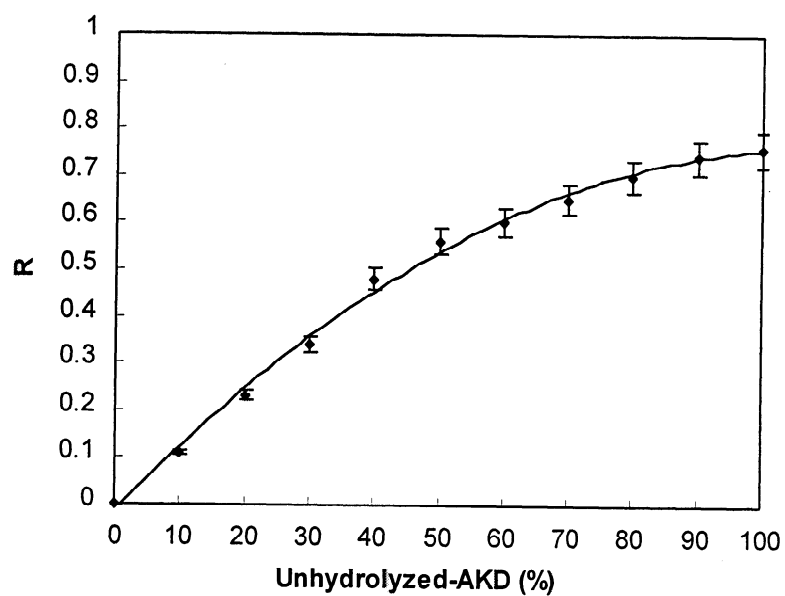


Figure 3. Standard calibration curve. R is the ratio of peak α at 1848 cm^{-1} to peak β at 1468 cm^{-1} .

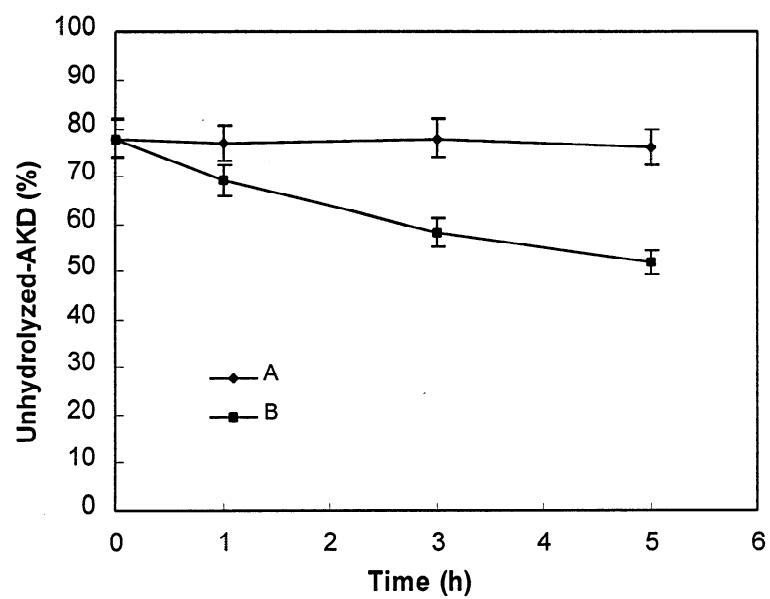


Figure 4. Temperature effect on the hydrolysis of AKD at pH 8.3.

A, 22 °C, and B, 50 °C.

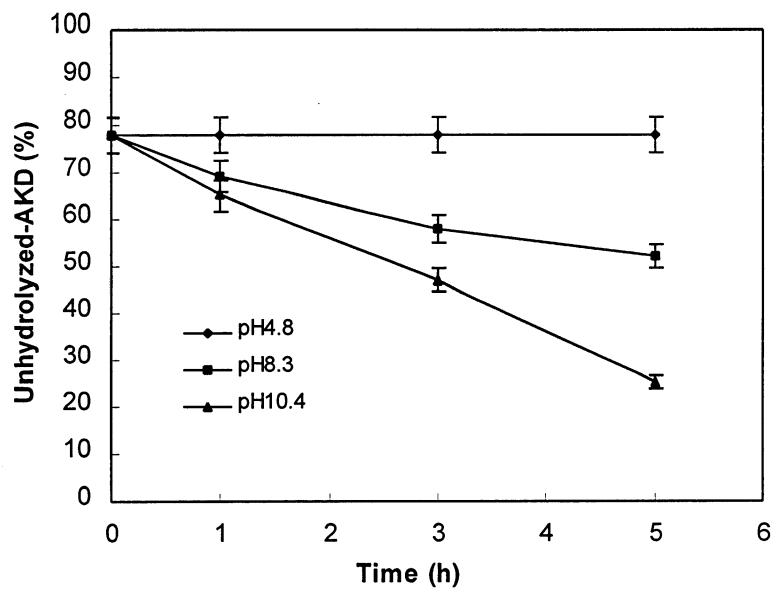


Figure 5. The pH effect on the hydrolysis of AKD at 50°C.

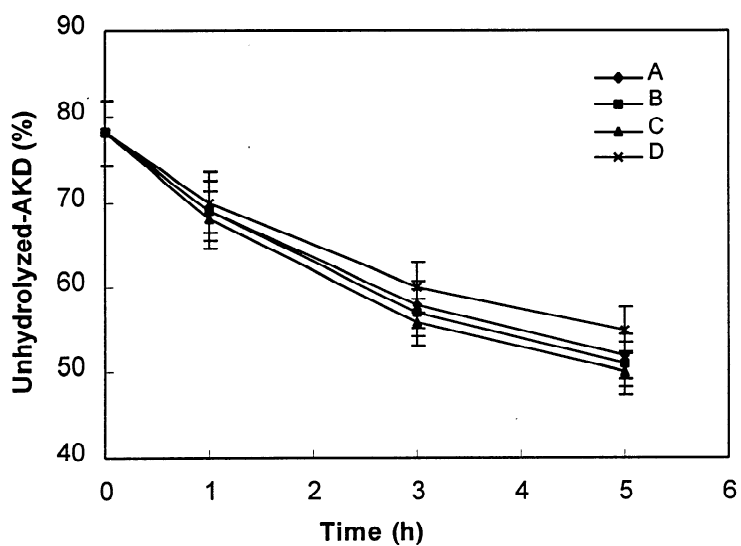


Fig. 6. The effect of inorganic salts on the hydrolysis of AKD at 50°C and pH 8.3.

A: pure AKD emulsion; B: AKD emulsion with 6000 mg/L Na_2SO_4 ; C: AKD emulsion with 1000 mg/L CaCl_2 ; D: AKD emulsion with 3000 mg/L NaCl +3000ppm Na_2SO_4 +1000 mg/L CaCl_2 .

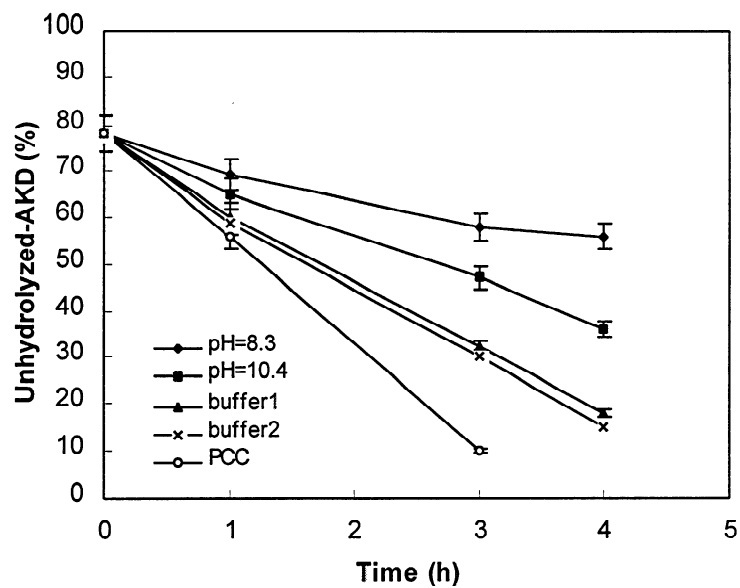


Figure 7. The effect of buffer solutions on the hydrolysis of AKD at 50°C. Buffer 1: 0.1M $\text{KH}_2\text{PO}_4 + \text{NaOH}$; Buffer 2: 0.1M $\text{NaHCO}_3 + \text{NaOH}$; PCC: 0.1 M PCC suspension. All of the solutions were adjusted to pH 8.3.

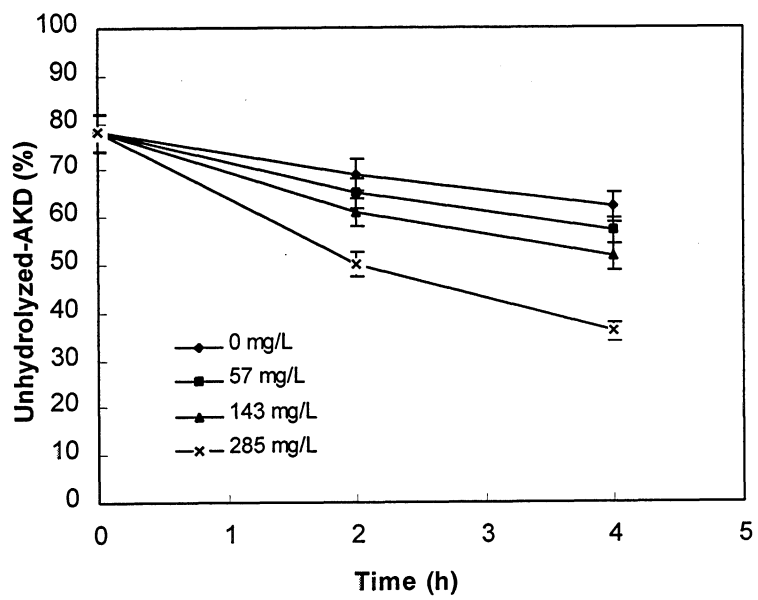


Figure 8. The effect of NaHCO_3 (mg/L) on the hydrolysis of AKD at 50°C, pH 7.9.

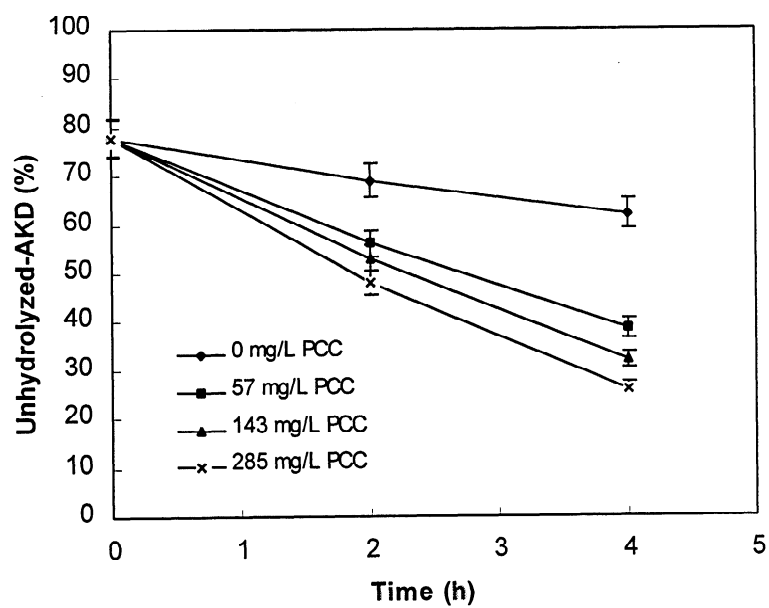


Figure 9. The effect of PCC (mg/L) on the hydrolysis of AKD at 50°C, pH 7.9.

